Proceedings of the American Academy of Arts and Sciences.

Vol. 64. No. 2.—December, 1929.

THE ELASTIC MODULI OF FIVE ALKALI HALIDES.

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Presented Oct. 9, 1929. Received Nov. 7, 1929.

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Introduction.

A knowledge of the elastic moduli of crystals is of much theoretical importance, but comparatively few have been determined. Perhaps the simplest of all crystals from the point of view of lattice structure are the alkali halides, but of these the elastic moduli only of NaCl have been determined at all satisfactorily, and of the others, determinations have been made on only two samples of KCl, of which one was obviously imperfect. The difficulty is in obtaining single crystals free from flaws in large enough pieces; the conditions are very much more exacting than in determining the cubic compressibility, for example.

By a development of the method which I have used for the production of single crystals of the metals,[1] it has been possible to produce single crystals of five alkali halides, namely NaCl, NaBr, KCl, KBr, and KI, large enough to permit cutting from them rods on which measurements of the elastic moduli could be made.

Methods.

Method of Making the Crystals. The method is that of slow cooling from the melt, the material to be crystallized being placed in a suitable mold, and slowly moved from the interior of a furnace maintained above the melting temperature to an external colder region. The

greatest difficulty in extending this method from metals, for which it works easily, to salts, is the great propensity of salts to crack into small pieces on cooling to room temperature. This is an effect of temperature contraction combined with the great brittleness of the salts. Temperature contraction may result in cracking either when the salt sticks to the walls of the mold, or when there is too steep a temperature gradient while withdrawing from the furnace. The difficulty with steepness of gradient can to a large extent be avoided by suitable design, but it is not possible to reduce the gradient indefinitely without danger that the isothermal surface at the solidifying temperature have more than one sheet, when crystallization may start from more than one nucleus. The difficulty from sticking to the walls of the mold was in large part avoided by making the mold of platinum foil 0.001 inch thick, as was first done by Ramsperger and Melvin.[2]

In order to determine the elastic constants it was necessary to get the specimen into the form of a slender rod. In order to avoid casting large blocks in single crystal form from which the rods could be cut, the casting was made at once in the form of a rod. The natural method would be to make the mold in the form of a thin tube, like the glass capillaries in which the metals were cast, but this did not prove successful. There were difficulties in making the mold out of the thin foil, but the greatest difficulty was in getting the casting out of the mold without cracking it. Finally the molds were made in the form of open boats, used in a horizontal position. This demanded, of course, that the axis of the furnace be placed horizontally rather than vertically. The boats were bent from pieces of foil 8.3 cm long and 1.9 cm wide; the ends were welded together, and the edges bent double to increase the transverse stiffness. At first the joints in the boats were made with pure gold solder, but this was given up because gold is soluble in the molten salts, and it was very difficult to use such a small quantity of gold as not to appreciably discolor them. One very important point in making the boats is that the platinum must be slightly crinkled, instead of being left perfectly smooth; the crinkling provides enough elastic yield to prevent the cracking which otherwise takes place. The cold casting could be removed from the boat without great difficulty by working the platinum foil away from the casting with the thumbs of the two hands simultaneously, as will readily suggest itself on trial. It was never possible to use the foil more than once. No substitute was

found for platinum, although several were tried. The most nearly successful was silver, but this slowly dissolves in the molten salt.

In the furnace the boats with their contents were protected from drafts and any furnace fumes by enclosing them in quartz test tubes, with stoppers ground so as not to be quite a perfect fit, thus allowing thermal expansion of the air within. Several of the quartz test tubes with their contents were made together into a bundle with a suitable holder, and withdrawn simultaneously from the furnace, so that several castings could be made at the same time.

The furnace was made in two parts with independent windings. In one half the temperature was maintained by a suitable current 10° or 20° above the melting temperature, and in the second part at a temperature somewhat below the melting temperature; the proper relation between the two temperatures had to be determined by trial. The temperatures of the two parts of the furnace were read on thermocouples, so connected with potentiometer circuits as to give a sensitivity of considerably better than a degree. Temperature was maintained constant within a degree or so by manual regulation during the process of withdrawal. Current was supplied by an independent generator of much constancy, so that the manual regulation was not difficult. The molds were drawn from the hot part to the colder part at a rate of the order of 10 cm per hour. When the mold was entirely in the colder part, the current was gradually cut down, and finally the furnace allowed to cool over night. Too rapid cooling after solidification was responsible for the loss of a number of crystals.

After the castings are removed from the mold, they must be checked to make sure that they are one grain. A simple way of doing this is to rub the surface of the casting lightly with a moist cloth, etching it slightly. When the moisture has dried off, it is very easy to tell by the appearance of the reflection pattern whether there is more than one grain. If the crystal passed this test, it was then formed into a slender cylinder. This was done in a jeweller's lathe, and of course required some care, but after some practice it was not difficult to get rods sometimes 5 cm long and 0.28 cm in diameter, round and true over the entire length to 0.0002 cm.

After the measurement of the elastic constants, to be described later, the orientation of the crystal axes was determined by making the principal cleavage planes with a knife blade, and measuring the angles with a protractor. The angles of all three planes were meas-

ured; the consistency of these three measurements thus furnished an internal check on the correctness of the orientation. The measured angles were adjusted so as to make the sum of the squares of the three direction cosines equal to unity, dividing the necessary adjustment among the angles proportionally roughly to the squares of the sines of the angles. The adjustment was practically never larger than a degree or two. The cleavage planes were determined at both ends of the rods, thus giving an additional check that the rods were truly one grain, and on the orientations.

The nature of the material will be described in detail in the presentation of data for the individual substances. One general remark is to be made, namely that slight and obscure impurities play a much more important part than I appreciated at first. In several cases a long series of unsuccessful results with salt from one source was followed by immediate success when the material was replaced by salt from another source, of no greater presumptive purity. In some cases the original material contained enough water so that there was violent snapping and jumping about of the salt on heating to the melting temperature. These materials were dried by a preliminary fusion, either in quartz or in a platinum crucible. An especially effective method of preliminary treatment is to cast the salt by the regular procedure for making single crystals, melting it in a large quartz test tube and slowly lowering in a vertical position through the furnace. The lower part of the resulting block was usually as clear as glass, except for the numerous cracks, and this clear material was used in making the final castings in the platinum boat.

Measurements of the Moduli. A cubic crystal has three independent elastic moduli, so that at least three different measurements must be made. There is a great deal of latitude as to what these may be; if perfect accuracy were attainable, either three independent different sorts of elastic deformation might be measured on a single specimen, or measurements of the same sort of deformation, as a bending, for example, might be made on three different samples of different orientations. The experimental accuracy is far from perfect. however, so that many observations, of different kinds of deformation on different samples, were desirable. The sort of deformation that is easiest to measure is the bending and twisting of rods, and the measurements made in connection with this paper were of the bending and twisting of rods of a variety of orientations. In addition, the linear compressibility may be measured. This has already been

determined by Slater[3] for all the salts of this paper; it can be measured with high accuracy, is not much affected by imperfections in the specimen, and there are values by other observers against which the values of Slater may be checked. In calculating the elastic moduli from the data of this paper, I have assumed that Slater's values for the compressibility are correct.

The experimental determinations of bending and twisting were made by methods conventional enough not to need extended description. In determining the bending, the round rod was supported at each end on V-shaped knife edges, the distance between the end supports being about 2.5 cm. The load was applied to a scale pan slung from the center with a double loop of cotton thread. Pressed up by a spring against the under side of the rod at the center between the loops of thread was a link arrangement, by which any vertical displacement of the center was transmitted to a conventional rocking mirror. The two ends of the rod were pressed against the V-shaped notches by springs with greater force than the upward force on the link. The scale distance was about 4.5 m, and the width of the mirror rocker 0.11 cm, so that the magnification was about 8000. The load was applied to and removed from the pan with a spring arrangement to avoid shock. In most cases the load was 20 gm, but for two of the less deformable salts was 40 gm. The displacements of the scale observed in the telescope for this load were of the order of 1.5 cm, and this could easily be read to 0.1 mm. At first, readings were made at both half and full load. The reading with half load came out so consistently equal to half the reading with full load that continued check of this point seemed superfluous, and the later readings were made only with full load. The readings were made immediately after the application and removal of load, so that strictly these are measurements of the adiabatic moduli; the difference between adiabatic and isothermal modulus is disregarded in the following. The effective bending modulus of a round rod cut from a cubic crystal should be the same for all orientations of the rod about the axis; this was always checked by making readings on each rod for four orientations spaced 90° apart. At each orientation, five readings of the displacement under full load were made. The readings in different orientations did not always agree, but differed by only a few per cent, and in no consistent manner; the average of all the readings was taken in calculating the effective bending modulus.

The twist was determined with apparatus that had already been used in determining the twist of slender single crystal rods of the metals. The specimen is held rigidly at one end, and at the other end is attached to the arm through which the twisting couple is applied through an arrangement of knife edges so that the couple acts practically without friction. The maximum twisting moment applied to these rods was about 170 gm cm. The twist is observed in telescope and scale in two mirrors, attached by a spring arrangement of obvious enough design to the central part of the rod. The mirrors must be far enough from the ends of the rods to avoid end effects; the usual distance between the mirrors was of the order of 2 cm, and the clear length of the rod about 4 cm. The twist was determined from the difference of reading of the two mirrors. The proportionality between twist and moment was tested in every case, and no deviation found within experimental error, which might be perhaps as much as 1%. The scale was 4.5 m distant, and the difference of the two deflections of the order of 1 cm, and the optical system was good enough to permit the certain estimation of 0.1 mm. Ten or a dozen readings of the twist of each rod were usually made, and the average taken.

The rods were attached to the two end pieces with cement. At first, elaborate precautions were taken not to heat the rods in applying the cement more than a few degrees, and paraffine and other low melting substances were used as cement. These were all unsatisfactory, and many times the specimen slipped. Finally it was found that these slender rods can stand much apparent abuse, and they were cemented into the holders with deKhotinski cement, melted into position with a small gas flame, which many times fell directly on the specimen without cracking it. It is surprising how difficult it is to crack one of these rods by unequal heating. I hoped to be able to get the cleavage planes by a local heating, instead of fracturing with a knife blade, but without success. Cooling in liquid air was also ineffective in producing the desired fracture. There must, however, judging by the behavior of the specimens as they come from the furnace, be a region near the melting point where the salt is very brittle and very sensitive to temperature inequalities.

The fundamental elastic moduli are connected with the bending and twisting moduli by formulas which may be found in Voigt.[4] For the bending of a round bar, we have the formulas:

$$u = \frac{WL^3 s_{33}'}{12\pi a^4}, \tag{1}$$

$$s_{33}' = s_{11} - 2\{s_{11} - s_{12} - \tfrac{1}{2}s_{44}\}\{\gamma_2^2\gamma_3^2 + \gamma_3^2\gamma_1^2 + \gamma_1^2\gamma_2^2\}. \tag{2}$$

Here u is the displacement under the weight W of the center of the rod, the length of which is L and the radius a. γ_1, γ_2, and γ_3 are the direction cosines of the three crystal axes referred to the length of the rod. s_{11}, s_{12}, and s_{44} are the three elastic moduli to be determined, referred in the conventional way to the principal crystal axes. That is, stress and strain are connected by the relations:

$$\left.\begin{aligned} e_{xx} &= s_{11}X_x + s_{12}Y_y + s_{12}Z_z \\ e_{yy} &= s_{12}X_x + s_{11}Y_y + s_{12}Z_z \\ e_{zz} &= s_{12}X_x + s_{12}Y_y + s_{11}Z_z \end{aligned}\right\} \qquad \left.\begin{aligned} e_{yz} &= s_{44}Y_z \\ e_{zx} &= s_{44}Z_x \\ e_{xy} &= s_{44}X_y \end{aligned}\right\}.$$

For the twist we have:

$$n = \frac{N}{\pi a^4}(s_{44}' + s_{55}'), \tag{3}$$

$$(s_{44}' + s_{55}') = 4(s_{11} - s_{12}) - 4\{s_{11} - s_{12} - \tfrac{1}{2}s_{44}\}\{\gamma_1^4 + \gamma_2^4 + \gamma_3^4\}. \tag{4}$$

Here n is the twist per unit length, and N is the twisting moment.

Also, the cubic compressibility χ is given by:

$$\chi = 3(s_{11} + 2s_{12}). \tag{5}$$

We now have the problem of determining the best values for the three moduli s_{11}, s_{12}, and s_{44} from measurements on a large number of specimens. Equation (1) may be solved for s_{33}' in terms of the dimensions and the measured displacement u, and (3) may be solved for $s_{44}' + s_{55}'$ in terms of twist and dimensions, and these values substituted in (2) and (4). The result of this is two linear equations in the three unknown moduli, the coefficients being known functions of the orientations. Next, taking the compressibility as known from equation (5) express s_{12} in terms of the known compressibility and s_{11}. Substituting this value for s_{12} back into (2) and (3) gives two linear equations in the two moduli s_{11} and s_{44}, the coefficients being function of the orientations, displacements, and compressibility. Finally, by dividing these equations through by the constant term, they may be written in the form:

$$a_{11}s_{11} + a_{12}s_{44} = 1, \text{ (6), from bending measurements.}$$

$$a_{21}s_{11} + a_{22}s_{44} = 1, \text{ (7), from twisting measurements.}$$

For any particular rod, after the measurements have been completed, the values of a_{11} and a_{12} are known from the measurement of bending, or a_{21} and a_{22} from the measurements of the twist. But whatever the values of a_{11} etc., they must be consistent with a single definite pair of values of s_{11} and s_{44} when substituted into (6) or (7). But now if we regard a_{11} etc. as variables, then (6) or (7) is the equation of straight line with intercepts $1/s_{11}$ and $1/s_{44}$, the intercepts, and hence the line represented, being the same for either (6) or (7). Writing (6) or (7) in the common form

$$a_1 s_{11} + a_2 s_{44} = 1, \tag{8}$$

the following procedure is at once suggested. From the measurements of elastic distortion, dimensions, and orientation, obtain for each specimen an equation in the form (8). Plot the coefficients a_1 and a_2 as points in an $a_1 - a_2$ plane. There will be as many of these points as there are independent measurements of elastic distortion. These points must all lie on the same straight line, the intercepts of which on the axes are $1/s_{11}$ and $1/s_{44}$. The best values for the moduli from a number of independent measurements I assume to be given by the intercepts of the best line that can be drawn through all the points, and the internal consistency of the measurements on different samples is shown by the accuracy with which the points lie on a single line.

It is obvious that the greatest accuracy would be obtained by so locating the points as to lie as near the axes as possible. An inspection of the equations shows at once what this involves. If one of the principal axes lies along the length of the rod, only s_{11} occurs in (2), and only s_{44} in (4), so that bending and twisting measurements on rods of these orientations would give directly s_{11} and s_{44}. Unfortunately, this orientation is one that does not often spontaneously occur, but the rods naturally grow from the melt in intermediate directions, as will be apparent from the detailed presentation of the data. Only in the case in which I repeated Voigt's measurements on NaCl cut from large natural blocks was the most favorable orientation exactly attained.

Detailed Data.

KI. This was the first substance attempted, and much more time was spent on it than on any of the others. A considerable part of the time was spent in finding the various best details of the

method. All the early work was done with material from Kahlbaum, of the highest purity which they manufacture, but not their "K" grade. I anticipated that KI would be the easiest of all the materials to crystallize, because Slater had found it so, but although a great many attempts were made, only five specimens in all were obtained on which it was possible to measure the elastic distortion. Even these specimens were not all satisfactory, as it was not always certain that the specimens were truly one grain, and the results were very scattering. After no further improvement in the technique seemed easily possible, this material was given up, somewhat in despair, and KBr tried, which was obtainable in Kahlbaum's "K" grade. The first attempt was brilliantly successful. The obvious explanation of the difference was in the difference of purity of the two materials, and it therefore became important to obtain KI of greater purity. Finally I was fortunate to obtain some of the old stock of Powers, Weightman, and Rosengarten, now no longer manufactured. This proved adequate, giving clear castings with sharp cleavage planes from which the rods were readily machined in the lathe. To a cutting tool the consistency of KI is much like that of horn or celluloid; in progressing through the series of halides toward smaller atomic weights the hardness and accordingly the difficulty in turning increases.

Five specimens were made with the pure material, which gave good single crystals and satisfactory determinations of the elastic moduli. The results obtained with these five specimens, and also with the best of the Kahlbaum material, are shown in Figure 1, the coefficients of s_{11} and s_{44} being plotted in the way already described. The points all lie on a straight line within the limits of error. In determining these coefficients Slater's value used for the compressibility was 8.54×10^{-12} Abs. C. G. S. It is unfortunate that the orientations were not more favorably distributed. It will be seen that only one of the specimens approximately satisfied the condition of most favorable orientation with one cleavage plane perpendicular to the length. The method used for producing the crystals gives no direct control of the orientation, although it might be modified to do so, and one has to trust more or less to luck to get what is needed. A number of other perfect single grain specimens were made in addition to those measured, in an endeavor to get some with more favorable orientations, but without success.

An attempt was made to determine the effective Young's modulus,

that is, the modulus s_{33}', directly by measuring the extension when stretched by a weight, but the shortness of the specimen made it difficult to eliminate various irregularities arising from the end

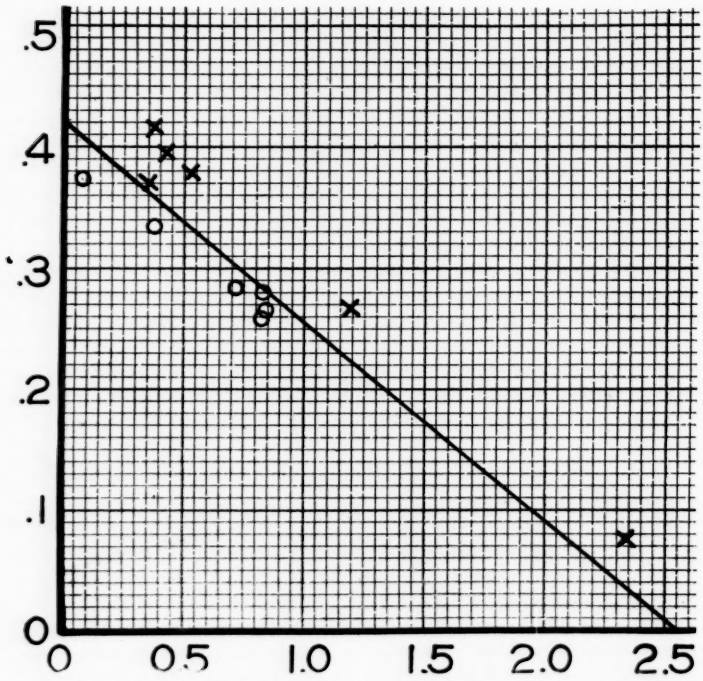

Figure 1. The coefficients of $s_{11} \times 10^{-11}$ in equation 8 plotted as abscissas against the coefficients of $s_{44} \times 10^{-11}$, for potassium iodide. The points obtained from bending measurements are shown as crosses, and those from twisting measurements as circles. If there were no experimental error the points should all lie on a straight line.

effects, and the attempt was abandoned in favor of the more convenient method by bending.

KBr. The material used was Kahlbaum's, grade "K," as has already been explained. Measurements were made on eight speci-

mens, of which only three were measured for torsion. It is more difficult to get a good specimen for the torsion measurements than for bending, because the length must be greater.

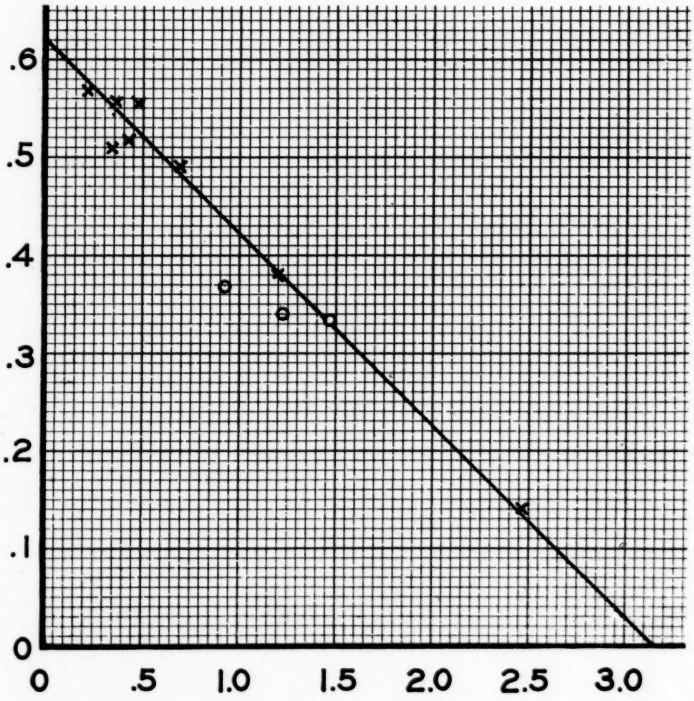

Figure 2. The coefficients of $s_{11} \times 10^{-11}$ in equation 8 plotted as abscissas against the coefficients of $s_{44} \times 10^{-11}$, for potassium bromide. The points obtained from bending measurements are shown as crosses, and those from twisting measurements as circles.

The coefficients of s_{11} and s_{44} are plotted in Figure 2, and again it will be seen that the points lie on a straight line, as is demanded by the crystal symmetry. Slater's value for the compressibility of KBr is 6.69×10^{-12}.

KCl. This was from Kahlbaum, grade "K." In spite of the high melting point, this was distinctly the easiest to work with of the materials tried. The rods were beautifully clear, always one grain, long enough for the torsion measurements, and of considerable

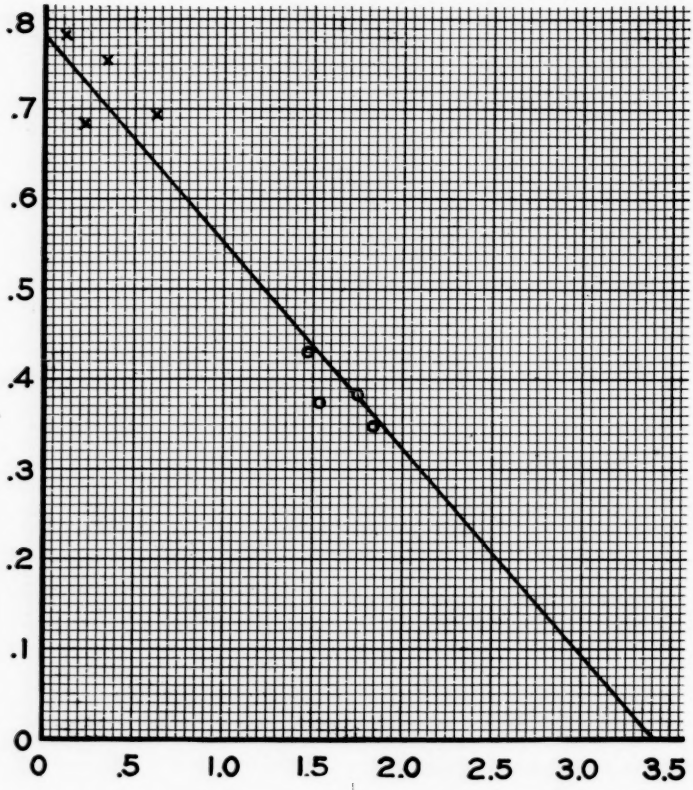

Figure 3. The coefficients of $s_{11} \times 10^{-11}$ in equation 8 plotted as abscissas against the coefficients of $s_{44} \times 10^{-11}$, for potassium chloride. The points obtained from bending measurements are shown as crosses, and those from twisting measurements as circles.

mechanical strength, so that turning was an easy process. Bending and torsion measurements were made on four specimens; the coefficients of s_{11} and s_{44} are plotted in Figure 3. The points lie on a straight line within the limits of error. Slater's compressibility is 5.64×10^{-12}.

NaBr. Attempts to prepare single crystals of this from the purest material that I could purchase were not successful. Professor Baxter was, however, so kind as to have prepared from his stock of atomic weight material some of this salt of unusual purity. Enough of the pure material was available for three crystals; all of this was cast successfully as single grains. Unfortunately the one of these which would have given the most accurate information, with a cleavage plane nearly perpendicular to the length, broke in turning. This, of course, is much more likely to happen when the cleavage plane is perpendicular, an exasperating situation. Satisfactory measurements were made of the bending and twist of the two remaining specimens, and the results are shown in Figure 4, plotted in the regular way. The 40 gm. weight, instead of that of 20 gm., was used in making the bending measurements. Slater's compressibility for this is 5.08×10^{-12}.

NaCl. These measurements were made mostly by way of check, there being no a priori reason to think that the material on which Voigt worked was not satisfactory. The material used was natural rock salt, which can be obtained in large clear blocks. In addition to the natural material one single grain specimen was prepared by crystallization from the melt from salt of Powers, Weightman and Rosengarten. The bending and twisting of this specimen was measured, and also its compressibility, as will be described later.

The natural crystal blocks were of German origin, obtained through Ward's Natural History Establishment. Three rods were cut from one block, and two from another. They were cut perpendicular to the cleavage planes, so that bending and twisting measurements gave directly s_{11} and s_{44}. Three rods from the first block gave for s_{11} .216, .209, and $.212 \times 10^{-11}$ respectively, and the two from the second: .230 and $.232 \times 10^{-11}$. It would thus appear that there are differences between the elastic moduli of rods cut from different blocks greater than the experimental error. This result emphasizes a conclusion that has been becoming increasingly evident lately, namely that it is very seldom that natural crystals are the unique things that have been supposed. Twisting measurements were made on only one rod from each block; these gave for s_{44} .782 and

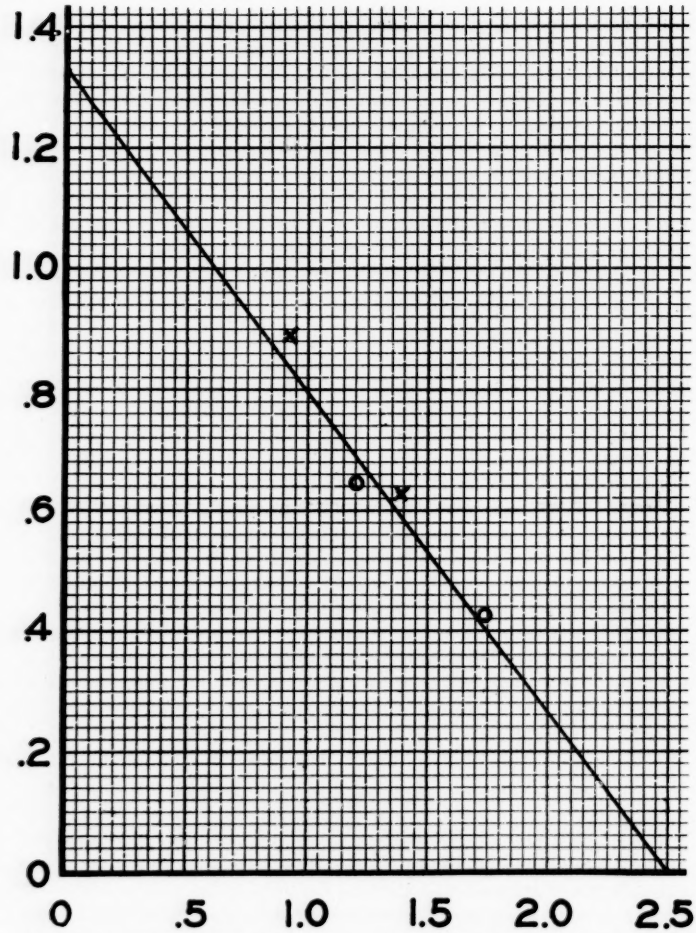

Figure 4. The coefficients of $s_{11} \times 10^{-11}$ in equation 8 plotted as abscissas against the coefficients of $s_{44} \times 10^{-11}$, for sodium bromide. The points obtained from bending measurements are shown as crosses, and those from twisting measurements as circles.

$.742 \times 10^{-11}$ respectively. The values which Voigt gives for natural NaCl are: $s_{11} = .243 \times 10^{-11}$, $s_{12} = -.0527 \times 10^{-11}$, $s_{44} = .788 \times 10^{-11}$. In the following I have selected as the most probable values: $s_{11} = .23 \times 10^{-11}$ $s_{12} = -.05 \times 10^{-11}$, $s_{44} = .78 \times 10^{-11}$. The values of bending and twist of the sample crystallized from the melt were not inconsistent with these values. The orientation was not favorable, however, so that no weight can be attached to the values of the moduli which would be given by a rigorous calculation from the two measurements.

The compressibility of the sample crystallized from the melt was measured in the regular way to a maximum pressure of 12000 kg/cm^2 at 30° and 75° C, and the following results found:

$$\left.\begin{aligned} &\text{At } 30°, -\Delta V/V_0 = 41.82 \times 10^{-7}\, p - 50.4 \times 10^{-12}\, p^2 \\ &\text{At } 75°, -\Delta V/V_0 = 43.44 \times 10^{-7}\, p - 51.9 \times 10^{-12}\, p^2 \end{aligned}\right\}.$$

Here pressure is expressed in kg/cm^2 units, as in all my compressibility measurements. The average deviations of single readings from a smooth curve at these two temperatures were 0.13 and 0.21 % respectively, which is about the average accuracy for material of this nature.

There is some interest in this compressibility measurement since nearly all previous measurements of the compressibility of NaCl, of which there have been a number, have been made on the natural crystal. One would expect the artificial material, which starts with a chemical of known high purity, to be more pure than the natural material, and hence the compressibility measured with it to be more significant.

The compressibility values just given yield, when converted into Abs. C. G. S. units:

$$\left.\begin{aligned} &\text{At } 30°, -\Delta V/V_0 = 4.263 \times 10^{-12}\, P - 5.23 \times 10^{-23}\, P^2 \\ &\text{At } 75°, -\Delta V/V_0 = 4.428 \times 10^{-12}\, P - 5.38 \times 10^{-23}\, P^2 \end{aligned}\right\}.$$

Slater's value for the natural crystal at 30° was $4.20 \times 10^{-12}\, P - 4.60 \times 10^{-23}\, P^2$, and at 75° $4.33 \times 10^{-12}\, P - 4.74 \times 10^{-23}\, P^2$. The second degree formulas just given were calculated by me from Slater's results, which were tabulated in somewhat different form. The difference between the results of Slater and me is not large, but the sign of the difference is unexpected, the natural crystal being initially less compressible. The difference between the two results is not as

great as would appear at first, there being a compensation between the first and second degree terms; the total volume change at the maximum pressure of 12000 kg/cm² given by Slater's formula is not quite ½ % *greater* than given by mine.

The initial compressibility at 20° of the artificial crystal is 4.23×10^{-12} by extrapolation from my formula above, and 4.17×10^{-12} by extrapolation from Slater's for the natural crystal. The value of Adams, Johnston, and Williamson[5] for the natural crystal at the same temperature was 4.12×10^{-12}, and that of Madelung and Fuchs[6] 4.14×10^{-12}. Richards[7] is the only observer who has previously measured the compressibility of both the natural and the artificial crystal, and he finds the natural crystal somewhat *more* compressible, but since he gives only two significant figures for the natural crystal and three for the artificial, it is probable that too great significance should not be attached to this difference. His value for the artificial material was 4.30×10^{-12} and 4.5 and 4.6×10^{-12} for two samples of the natural crystal. Both his values are distinctly larger than those of other observers.

The maximum variation in compressibility between any of the observed values is not great enough to introduce appreciable changes in the values given for the moduli as calculated from observations on bending, twist, and compressibility.

Other Salts. Unsuccessful attempts were made to crystallize some of the other alkali halides, but no great effort was expended on these, and others should not be deterred by my failure. The lithium salts are difficult to manage either because they are very hygroscopic, or because they cannot be obtained in sufficient purity. NaI could not be obtained in sufficient purity. Professor Baxter was so kind as to partially purify my commercial material by recrystallization from aqueous solution. This treatment would be expected to remove any organic impurities, but this did not prove to be sufficient. RbCl was also attempted; I had a very small supply left from the material prepared by Professor Richards, the polymorphic transitions of which under pressure I had measured. Dr. Paul Anderson was so kind as to remove by electrolysis the iron which had got into it during the pressure manipulations, but this did not prove to be sufficient.

Summary and Discussion.

In the following table are given the values of the elastic moduli obtained from the compressibilities and the intercepts on the axes

of the lines already shown in the figures for the various salts. The number of significant figures given for NaCl is less than for the others because of the uncertainty arising from the variation in the different samples of the natural crystal.

TABLE.

ELASTIC MODULI IN ABS. C. G. S. UNITS.

Salt	s_{11}	s_{12}	s_{44}
NaCl	$.23 \times 10^{-11}$	$-.05 \times 10^{-11}$	$.78 \times 10^{-11}$
NaBr	.400	−.115	.754
KCl	.294	−.053	1.27
KBr	.317	−.047	1.61
KI.	.392	−.054	2.38

The most important question in connection with these elastic moduli, and which was decisive in my decision to attempt their measurement, is whether Cauchy's relation holds. Expressed in terms of the elastic constants this is $c_{12} = c_{44}$; in terms of the moduli it is more complicated, being

$$(s_{11} - s_{12})\,(s_{11} + 2\,s_{12}) = -\,s_{12}\,s_{44}.$$

In the case of the general crystal the relations of Cauchy are more complicated, and reduce the 21 constants required by general considerations of thermodynamics and crystal symmetry to 15. These relations were deduced by Cauchy on the assumption that the forces between the elements of the crystal structure have spherical symmetry. It is known that in general the relations cannot be correct, as shown by the experimental measurement of the elastic constants of a large number of different crystals by Voigt. An adequate theoretical account is given of the situation by Born's theory of crystal lattices;[8] the failure of the Cauchy relation is shown to be connected with the possibility of a rigid relative displacement with respect to each other of the elementary lattices of which the crystal is composed. The fact that Cauchy's relation does not apply to cubic crystals of the metals must be taken, according to Born's theory, to mean that the displacements of the atomic nuclei relative to the surrounding cloud of electrons play an essential part in the elastic phenomena of metals. The situation is simpler with regard to the alkali halides than with regard to the metals. If the alkali halide structure can be adequately represented by interpenetrating

cubic lattices of positive and negative ions, the attractive forces being the electrostatic forces and the repulsive forces some high inverse power of the distance, then Born's theory reduces to Cauchy's, so that the Cauchy relation should hold. Now there is considerable physical evidence, apart from the elastic behavior, to suggest that this is an adequate picture of the interatomic forces, and consequently the expectation is that the Cauchy relation will hold. The expectation that the relation will hold is much strengthened by the new wave mechanics,[9] because according to this a complete electron shell must have perfect spherical symmetry, and not the sort of cubic symmetry that Born at first supposed, and furthermore the ions of the lattice are composed of complete shells.

The experimental check of the Cauchy relation has, however, been meagre. The only satisfactory material hitherto available has been NaCl, for which the measurements of Voigt[10] showed the relation satisfied. Voigt[10] also measured KCl, but his material was not satisfactory in that only two specimens were available, not perfectly free from flaws. The values of the elastic constants obtained from the two specimens of KCl were quite different. Voigt was inclined to take the average of the constants from the two specimens as giving the most probable value, in which case the Cauchy relation was far from satisfied. Försterling[11] remarked, however, that one of Voigt's specimens was evidently much poorer than the other, because the cubic compressibility calculated from its elastic constants failed by a large amount to agree with the direct experimental value of other observers, whereas the other specimen gave agreement. Discarding the poorer sample, the other sample of KCl approximately satisfied Cauchy's relation. In general, therefore, the experimental check could not be called satisfactory. It was still less satisfactory when it is considered that NaCl and KCl might give a fortuitous check because of their position somewhere near the middle of the alkali halides series, whereas the more extreme members of the series might not give a check. A very similar situation arose with respect to the inverse ninth power of repulsive force demanded by Born's original theory of compressibility; the ninth power was found for NaCl, but not for the extreme members of the alkali halide series.

The following procedure was adopted in examining experimentally whether the Cauchy relation holds for the salts measured above. It will be remembered that, assuming the experimental determination

of compressibility to have higher accuracy than the other elastic moduli, the results of the bending and twisting measurements on rods of different orientations could be plotted in such a way that all points must lie on a single straight line. The intercepts of this line determined the moduli s_{11} and s_{44}. In general, there is no necessary connection between s_{11} and s_{44}, so that a two-parameter family of lines is available to represent the results. But if the Cauchy relation holds, there is an additional relation between the moduli, so that if s_{11} is given, s_{44} is determined, and the possible straight lines by which the experimental results can be represented become a one-parameter family. In detail, $s_{12} = \frac{1}{2}(k - s_{11})$ where k is the linear compressibility, and substituted into the Cauchy relation this gives

$$s_{44} = \frac{k(3s_{11} - k)}{s_{11} - k}.$$

This determines the s_{44} intercept when the s_{11} intercept and the compressibility are fixed.

The lines given in all figures have been drawn subject to this restriction. Although in each of the figures it is probable that exactly the line shown would not have been drawn if a least squares determination had been made of the best line for each figure taken by itself, nevertheless in each case the line shown comes very close to the line that would have been drawn with no ulterior consideration. Hence the conclusion may be drawn that the Cauchy relation is satisfied at least very closely by all the salts, and there is no reason to think that it may not be satisfied within a considerably smaller margin than the error of these experiments. As a first approximation, the assumption of the Cauchy relation seems to be justified.

Although the theory is thus justified as far as the Cauchy relation goes, it is still very far from complete. A complete theory would allow a detailed calculation of the numerical values of all three moduli. This it was not able to do in the case of NaCl, and the situation is not altered now by the determination of these new constants. In fact, the situation has become somewhat more complex, because although there is a certain regularity in the progression of the compressibility in passing from one alkali halide to another, and there is also a regularity in s_{11}, there is no such regularity in s_{12} and s_{44}, whereas some sort of regularity would doubtless be given by any first simple theory.

Summarizing, the three elastic moduli of KI, KBr, KCl, NaBr,

and NaCl have been determined, and the compressibility of an artificial crystal of NaCl measured to 12000 kg/cm^2. The Cauchy relation between the elastic moduli is found to be satisfied, thus checking the expectation from Born's theory of crystal lattices, now put on a firmer basis by the new wave mechanics. There is, however, no theory which gives the exact numerical values of the moduli; there are irregularities in the sequence of the moduli which will probably be difficult for a simple theory.

It is a pleasure to acknowledge the skillful assistance of Mr. George Langreth in the manipulations of producing the single crystals. I am also much indebted for financial assistance to the Milton Fund of Harvard University.

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